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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

ms

To:

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CARPMAELS & RANSFORD
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London WC1A 2RA
GRANDE BRETAGNE

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)

Date of mailing
(day/month/year) 24.02.2000

Applicant's or agent's file reference
JFF/D 3791

IMPORTANT NOTIFICATION

International application No.
PCT/GB98/03695

International filing date (day/month/year)
10/12/1998

Priority date (day/month/year)
11/12/1997

Applicant
DE BEERS INDUSTRIAL DIAMOND DIVISION... et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference JFF/D 3791	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) FOR FURTHER ACTION	
International application No. PCT/GB98/03695	International filing date (day/month/year) 10/12/1998	Priority date (day/month/year) 11/12/1997
International Patent Classification (IPC) or national classification and IPC B01J3/06		
Applicant DE BEERS INDUSTRIAL DIAMOND DIVISION... et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 9 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 		
Date of submission of the demand 16/06/1999	Date of completion of this report 24.02.2000	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Buesing, G Telephone No. +49 89 2399 8356	



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB98/03695

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

Description, pages:

6,9-16	as originally filed			
1-5,7,8	as received on	20/01/2000	with letter of	17/01/2000

Claims, No.:

1-7	as received on	20/01/2000	with letter of	17/01/2000
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Drawings, sheets:

1/3-3/3	as originally filed			
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2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application.
- ☒ claims Nos. 4 - 9.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB98/03695

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

see separate sheet

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1 -2
Inventive step (IS)	Yes:	Claims
	No:	Claims 3 - 7
Industrial applicability (IA)	Yes:	Claims 1 - 7
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB98/03695

Sections III and V:

1. Claims 1 and 2 lack novelty in view of D3 (identified below).
2. Claim 3 defines a method in so broad terms that no reasonable examination can be carried out; see also section VIII. Basically, claim 3 claims to make a mass of diamond crystals wherein source crystals are contacted with a solvent/catalyst and then subjected to suitable pressure and temperature conditions. As such processes are generally applied in the art for producing wear resistant materials, it appears that claim 3 lacks novelty.
3. Reference is made in this respect to the following documents:
D1: EP-A-0 079 117 (GENERAL ELECTRIC COMPANY) 18 May 1983
D2: HONGCHANG YU ET AL.: 'Sintering of Ultrafine Diamond Particles Under High Temperature and High Pressure' DIAMOND AND RELATED MATERIALS, vol. 3, no. 3, 1 February 1994, pages 222-226, XP000483447 LAUSANNE CH
D3: SHI MING HONG ET AL.: 'Diamond Formation from a System of SiC and a Metal' DIAMOND AND RELATED MATERIALS., vol. 2, 1993, pages 508- 511, XP000361192 AMSTERDAM NL
D4: US-A-4 551 316 (EIICHI IIZUKA) 5 November 1985

Section VIII:

1. Claims 3, 4, 6 and 7 are vague and indefinite because they do not define the process conditions needed for producing the material but merely indicate the desired results (eg in claim 3: "the conditions of crystal growth being chosen such that the source crystals are converted to crystals having developed macroscopic facets of low Miller index") or refer to an effect (claims 6, 7) without defining the process features that are necessary to obtain said effect.
2. It is observed that, contrary to the requirements of Rule 5.1 (a) (ii) PCT, there is no indication of background art in the description.
3. Attention is drawn to the copending application PCT GB98/03696 of the same applicant which relates to similar subject-matter.

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CRYSTAL GROWTH

BACKGROUND OF THE INVENTION

This invention relates to the growth of diamond, ~~cubic boron nitride and other~~ crystals under conditions of high temperature and high pressure.

The synthesis of crystals at high temperatures and high pressures, particularly diamond and cubic boron nitride, is very well established commercially. There are two principle methods employed, both from solution, namely a temperature gradient method and an allotropic change method. In the temperature gradient method, the driving force for crystal growth is the supersaturation due to the difference in solubilities of the source material and the growing crystal as the result of a temperature difference between the two. In the allotropic change method, the driving force for crystal growth is the supersaturation due to the difference in solubilities of the source material and the growing crystal as the result of an allotropic (or polymorphic) difference between the two.

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SUMMARY OF THE INVENTION

The present invention provides a mass of ~~crystals~~, particularly diamond crystals, which have a size of less than 100 microns and in which mass the majority of the crystals, and preferably at least 80 percent of the mass, are macroscopically faceted single crystals. Some of the crystals may be twinned.

A mass of ^{diamond}crystals, which are predominantly macroscopically faceted single crystals, may be produced by a method which includes the steps of providing a source of ^{diamond}crystals ~~[of the type to be grown]~~ and which are substantially free of macroscopically faceted surfaces, producing a reaction mass by bringing the source ^{diamond}crystals into contact with a suitable solvent/catalyst, subjecting the reaction mass to conditions of elevated temperature and pressure suitable for crystal growth in the reaction zone of a high temperature/high pressure apparatus, removing the reaction mass from the reaction zone and recovering the crystals from the reaction mass, the conditions of crystal growth being chosen such that the source ^{diamond}crystals are converted to ^{diamond}crystals having developed macroscopic facets of low Miller index. The mass of crystals will generally contain at least 80% of macroscopically faceted single crystals.

The method of generating the supersaturation driving force necessary for crystal growth used in the practice of this invention depends, at least in part, and preferably predominantly, upon the difference in surface free energy between low Miller index surfaces and higher Miller index surfaces.

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hereinafter referred to as "the Wulff effect"; higher Miller index surfaces having a higher surface free energy than lower Miller index surfaces. The equilibrium shape of a crystal occurs when the minimum total surface free energy per unit volume of crystal is attained, i.e. when the crystal is bounded by surfaces of low Miller index. Higher Miller index surfaces can be considered to comprise a series of stepped low Miller index surfaces in close proximity to one another. Such a situation is included in the term "higher Miller index surface". When a crystal is in its equilibrium shape, there exists a point whose perpendicular distance from every face is proportional to the surface free energy of that face. This is the basis of Wulff's theorem.

It has been found that in the case of diamond, ~~the preferred crystal in the practice of the invention~~ the difference in surface-free energy between high Miller index surfaces and low Miller index surfaces is large and can generate a supersaturation which sustains crystallisation when diamond crystals in various sizes, including those tens of microns in size, are used. Thus, the invention has particular application to the growth of diamond crystals wherein supersaturation is created, at least in part, and preferably predominantly, by a difference in solubility of crystal surfaces of high Miller index and crystal surfaces of lower Miller index, e.g. by the reduction of surface-free energy by the substantial elimination of steps, kinks and other structural defects which characterise macroscopic high Miller index surfaces.

It has further been observed that the Wulff effect is dependent on the conditions which prevail in the reaction mass. For example, for a given

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solvent/catalyst and pressure applied, the Wulff effect is dependent on temperature and time, as can be seen from the graphs shown in Figures 1 and 2. The graph of Figure 1 shows the temperature dependence of the Wulff effect on diamond in an iron-nickel solvent/catalyst at about 5,4 GPa, with this condition being maintained for one hour. The graph of Figure 2 shows the temperature dependence of the Wulff effect on diamond in the same iron-nickel solvent/catalyst at about 5,4 GPa with the condition being maintained for ten hours. From these graphs, it will be noted that the larger the source crystal size, the higher the applied temperature to ensure that the Wulff effect dominates and the production of a crystal mass containing a high proportion of single crystals having facets of low Miller index is achieved. Similar graphs can be produced for other solvent/catalysts and applied pressures to determine under what conditions the Wulff effect dominates.

Particles with a high portion of high Miller index surfaces will yield faceted ^{diamond} crystals more readily than particles with a low proportion of high Miller index faces. Further, particles with a low proportion of high Miller index surfaces may only facet partially and/or show dissolution facets.

~~[The conditions of elevated temperature and pressure for crystal growth will vary according to the nature of the crystal.]~~ For diamond crystals, the elevated temperature will generally be in the range 1100 to 1500°C and the elevated pressure generally in the range 4,5 to 7 GPa.

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The ~~crystals, particularly~~ diamond crystals~~x~~ may be recovered from the reaction mass using methods known in the art. For example, the most practical method is simply to dissolve away the solvent/catalyst leaving the mass of crystals. If some of the crystals are loosely bound to other crystals, they can be released by light milling or other similar action.

The method described above will primarily be used to produce a mass of crystals which has a size of less than 100 microns. However, the method may also be used for producing a mass of macroscopically faceted crystals of larger size and this also forms part of the invention.

The source ^{diamond}crystals may be provided by particles of irregular shape and substantially free of macroscopically faceted surfaces. An example of suitable source crystals is the product of a crushing operation. By way of example, Figure 4 shows a photograph at 260 x magnification of angular source diamond crystals. The source particles may also be provided by particles which have been treated so that macroscopic facets are damaged or destroyed, and/or surfaces of high Miller index are created, and higher surface energy faces formed thereby.

The source ^{diamond}crystals may have a narrow size distribution or a relatively wide size distribution. Provided the conditions are chosen such that the Wulff effect dominates in the crystal growth, then the mass of faceted single crystals produced will have essentially the same size distribution as that of the source crystals.

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DESCRIPTION OF EMBODIMENTS

The invention has application to the growth or synthesis of ^{diamond} ~~a range of~~ crystals which utilise high temperature and high pressure conditions. ~~The invention has particular application to the growth or synthesis of ultra-hard abrasive particles such as diamond and cubic boron nitride.~~

The size of the source crystals, will vary according to the nature of the crystal being grown.

The source crystals may also be provided by particles comprising a core of diamond and a coating of a suitable material such as a layer of a solvent/catalyst, provided, of course, that the diamond particle of the core has high Miller index surfaces and is substantially free of macroscopic facets.

The source crystals can also be provided by a particle comprising a core of any material having a cladding or coating of the crystal to be grown.

The solvent/catalyst which is used will depend on the nature of the crystal being grown. Examples of such solvent/catalysts in the case of diamond are transition metal elements such as iron, cobalt, nickel, manganese and alloys containing any one of these metals, stainless steels, superalloys (e.g. cobalt, nickel and iron-based), silicon steels, bronzes and brazes such as nickel/phosphorus, nickel/chromium/phosphorus and nickel/palladium. Other suitable solvent/catalysts for diamond synthesis are elements, compounds and alloys not containing transition metals. e.g. copper,

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copper/aluminium and phosphorus, and non-metallic materials or a mixture thereof such as alkaline, alkaline earth metal hydroxides, carbonates and sulphates, chlorates and silicates (such as hydrated forms of forsterite and enstatite).

In the case of diamond, the source particles may be synthetic diamond made by conventional high pressure/high temperature processes or other suitable technique, or natural diamond.

~~The conditions of elevated temperature and pressure which are used in the method will also vary according to the nature of the crystal being grown.~~ In the case of diamond ~~and cubic boron nitride~~ growth, the synthesis conditions may be those under which the crystal is thermodynamically stable. These conditions are well known in the art. However, it is also possible to produce diamond growth under conditions which are outside the region of thermodynamic stability of diamond. Conditions of temperature and pressure outside the region of thermodynamic stability of diamond can be used if the Ostwald rule dominates the growth process rather than the Ostwald-Volmer rule (see Bohr, R Haubner and B Lux Diamond and Related Materials volume 4, pages 714 - 719, 1995) - "According to the Ostwald rule, if energy is withdrawn from a system with several energy states, the system will not reach the stable ground state directly, but instead will gradually pass through all intermediate states. In addition, according to the Ostwald-Volmer rule, the less dense phase is formed (nucleated) first. Where the two rules would appear to contradict each other, the Ostwald-Volmer rule has priority over the Ostwald rule." In the case of diamond crystal growth outside its region of thermodynamic stability, the Ostwald-

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CLAIMS

1.

A mass of ^{diamond}crystals having a size of less than 100 microns and in which mass the majority of the ^{diamond}crystals are faceted single crystals.

2.

A mass of crystals according to claim 1 wherein at least 80% of the mass are faceted single crystals.

~~3.~~

~~A mass of crystals according to claim 1 or claim 2 wherein the crystals are diamond crystals.~~

~~4.~~ 3.

A method of producing a mass of ^{diamond}crystals, which are predominantly macroscopically faceted single crystals, including ^{ing} the steps of providing a source of ^{diamond}crystals ~~of the type to be grown~~ and which are substantially free of macroscopically faceted surfaces, producing a reaction mass by bringing the source into contact with a suitable solvent/catalyst, subjecting the reaction mass to conditions of elevated temperature and pressure suitable for crystal growth in the reaction zone of a high temperature/high pressure apparatus, removing the reaction mass from the reaction zone and recovering the crystals from the reaction mass, the conditions of crystal growth being chosen such that the source ^{diamond}crystals are converted to ^{diamond}crystals having developed macroscopic facets of low Miller index.

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~~5.~~ 4.

A method according to claim ~~4~~³ wherein the mass of ^{diamond} crystals contains at least 80% of macroscopically faceted single crystals.

~~6.~~

~~A method according to claim 5 wherein the crystals are diamond crystals.~~

~~7.~~ 5.

A method according to claim ~~8~~^{3 or claim 4} wherein the elevated temperature is in the range of 1100 to 1500°C and the elevated pressure in the range of 4,5 to 7 GPa.

~~8.~~ 6.

A method according to any one of claims ~~4 to 7~~^{3 to 5} wherein the supersaturation driving force necessary for crystal growth is generated predominantly by the difference in surface free energy between low Miller index surfaces and high Miller index surfaces of the source ^{diamond} crystals.

~~9.~~ 7.

A method according to any one of claims ~~4 to 8~~^{3 to 6} wherein the Wulff effect dominates.